Southeast Florida Utility Council

Chloramination Optimization Presentation

A review of chloramination theory and practices with the focus on optimizing distribution system reliability while minimizing tastes and odors, DBPs, and other complications associated with its use

November 14, 2016

Course Number: 05105131

(Course Approved By FS-AWWA for 1 PDH / 0.1 CEH)

carollo

Engineers...Working Wonders With Water®

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Agenda

1. What is chloramine?
2. Who uses chloramines?
3. Advantages and disadvantages of chloramines
4. Current DBPs
5. DBP formation
6. Controlling DBP formation
7. Future DBPs
8. Nitrification
9. Other effects
10. Free Chlorine burn conversion

What is Chloramine?

What is Chloramine?

Chlorine (Cl_2) + Ammonia (NH_3) = Mono Chloramine (NH_2Cl)

- Chloramines are used to provide ‘residual’ disinfection in water distribution pipelines
- Chloramines produce significantly less DBPs than chlorine on its own

Chloramine Chemistry is complicated

Table 7-1 – Monochloramine autodecomposition model

No.	Reaction	Rate or Equilibrium Constant	Reference
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$4.2 \times 10^6\ M^{-1}s^{-1}$	Jafvert and Valentine (1992)
2	$NH_2Cl + H_2O \rightarrow NH_3 + HOCl$	$2.1 \times 10^{-5}\ s^{-1}$	Morris and Isaac (1981)
3	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	$2.8 \times 10^2\ M^{-1}s^{-1}$	Margerum *et al.* (1978)
4	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	$6.4 \times 10^{-7}\ s^{-1}$	Margerum *et al.* (1978)
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	pH dependent*	Vikesland *et al.* (2001)
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	$6.1 \times 10^4\ M^{-2}s^{-1}$	Hand and Margerum (1983)
7	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H + 3Cl^-$	$1.5 \times 10^{-2}\ M^{-1}s^{-1}$	Leao (1981)
8	$NHCl_2 + H_2O \rightarrow NOH + 2HCl$	$1.1 \times 10^2\ M^{-1}s^{-1}$	Jafvert and Valentine (1987)
9	$NOH + NHCl_2 \rightarrow N_2 + HOCl + HCl$	$2.8 \times 10^4\ M^{-1}s^{-1}$	Leao (1981)
10	$NOH + NH_2Cl \rightarrow N_2 + H_2O + HCl$	$8.3 \times 10^3\ M^{-1}s^{-1}$	Leao (1981)
11	$HOCl \leftrightarrow H^+ + OCl^-$	$pK_a = 7.54$	Bodner and Pardue (1995)
12	$NH_4^+ \leftrightarrow NH_3 + H^+$	$pK_a = 9.24$	Bodner and Pardue (1995)
13	$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	$pK_a = 6.35$	Bodner and Pardue (1995)
14	$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	$pK_a = 10.33$	Bodner and Pardue (1995)

*$k_5 = kH^+[H^+] + kH_2CO_3[H_2CO_3] + kHCO_3^-[HCO_3^-]$ where $kH_2CO_3 = 11\ M^{-2}s^{-1}$, $kHCO_3^- = 0.22\ M^{-2}h^{-1}$, $kH^+ = 6944\ M^{-2}s^{-1}$

NOH is the unidentified monochloramine auto-decomposition intermediate

Table 7-2 – Important bromide – monochloramine reactions in drinking water treatment

No.	Reaction	Rate or Equilibrium Constant	Reference
15	$HOCl + Br^- \rightarrow HOBr + Cl^-$	$1.55 \times 10^3\ M^{-1}s^{-1}$	Kumar and Margerum (1987)
16	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$	$7.5 \times 10^7\ M^{-1}s^{-1}$	Wajon and Morris (1980)
17	$OBr^- + NH_3 \rightarrow NH_2Br + OH^-$	$7.6 \times 10^4\ M^{-1}s^{-1}$	Wajon and Morris (1980)
18	$NH_2Br + H_20 \rightarrow HOBr + NH_3$	$1.5 \times 10^{-3}\ s^{-1}$	Haag and Lietzke (1980)
19	$NH_2Br + NH_2Br \rightarrow NHBr_2 + NH_3$	pH dependent*	Lei *et al.* (2004)
20	$NHBr_2 + NH_3 \rightarrow NH_2Br + NH_2Br$	pH dependent^	Lei *et al.* (2004)
21	$NH_2Br + NHBr_2 \rightarrow N_2 + 3H^+ 3Br^-$	pH dependent+	Lei *et al.* (2004)
22	$NHBr_2 + NHBr_2 + H_2O \rightarrow N_2 + HOBr + 3H^+ + 3Br^-$	$8.9\ M^{-1}s^{-1}$	Lei *et al.* (2004)
23	$HOBr + NH_2Cl \rightarrow NHBrCl + H_2O$	$2.86 \times 10^5\ M^{-1}s^{-1}$	Gazda and Margerum (1994)
24	$OBr^- + NH_2Cl \rightarrow NHBrCl + OH^-$	$2.2 \times 10^4\ M^{-1}s^{-1}$	Gazda and Margerum (1994)
25	$NH_2Cl + NH_2Cl + Br^- \rightarrow NHBrCl + Cl^- + NH_3$	pH dependent#	Trofe *et al.* (1980); This work
26	$NHBrCl + NHBrCl + H_2O \rightarrow N_2 + HOBr + HBr + 2HCl$	$17\ M^{-1}s^{-1}$	Valentine 1983; This work
27	$HOBr \leftrightarrow OBr^- + H^+$	$pK_a = 8.8$	Haag and Hoigne (1983)

*$k_{19} = 0.5\ M^{-1}s^{-1} + 5 \times 10^8\ M^{-2}s^{-1}\ [H^+] + 290\ M^{-2}s^{-1}\ [NH_4^+] + 540\ M^{-2}s^{-1}\ [HCO_3^-]$

^$k_{20} = 1\ M^{-1}s^{-1} + 1 \times 10^9\ M^{-2}s^{-1}\ [H^+] + 190\ M^{-2}s^{-1}\ [NH_4^+] + 180\ M^{-2}s^{-1}\ [HCO_3^-]$

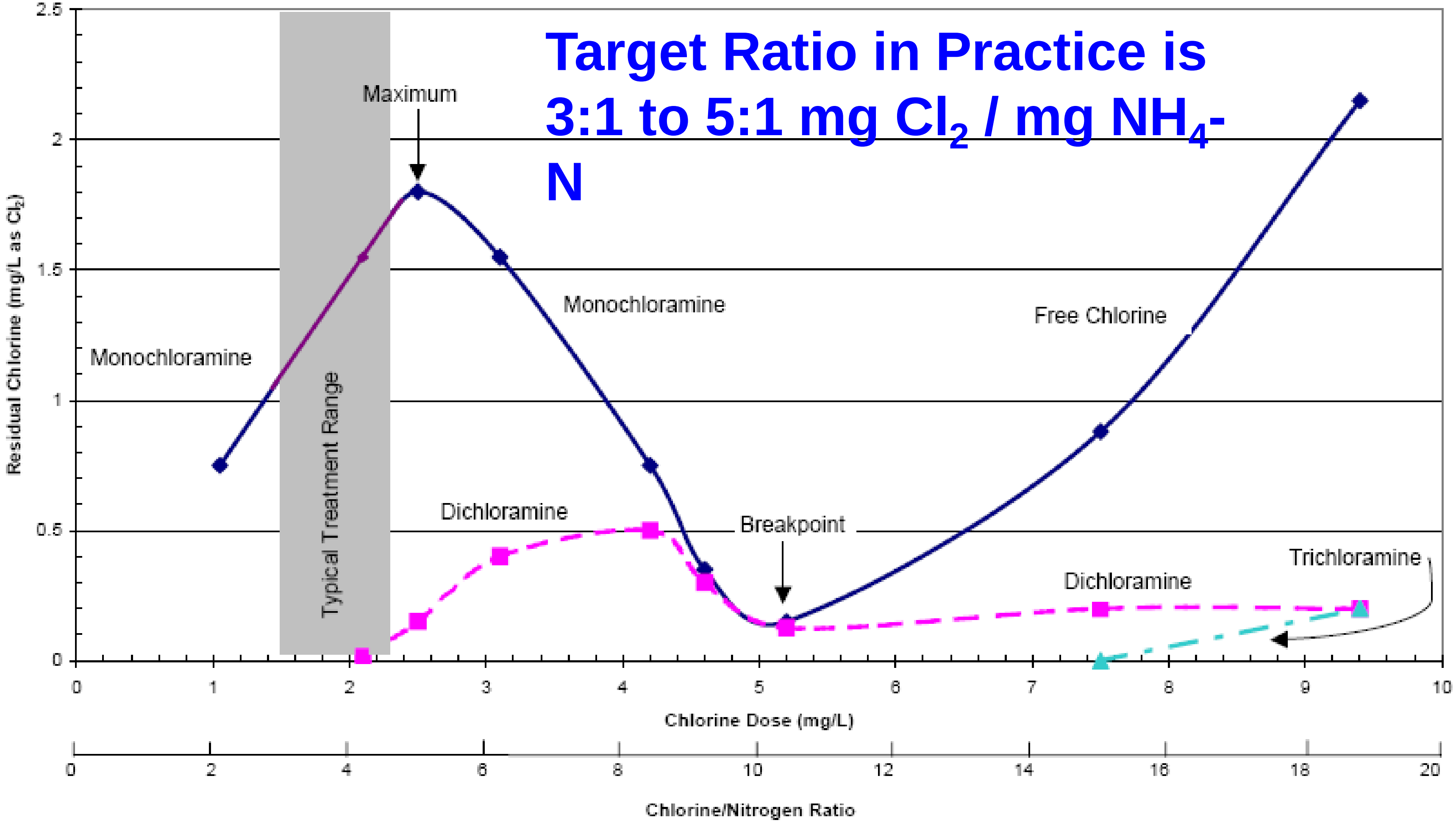
+$k_{21} = 6.2\ M^{-1}s^{-1} + 8.3 \times 10^4\ M^{-2}s^{-1}\ [OH^-] + 3.2 \times 10^3\ M^{-2}s^{-1}\ [CO_3^{2-}]$

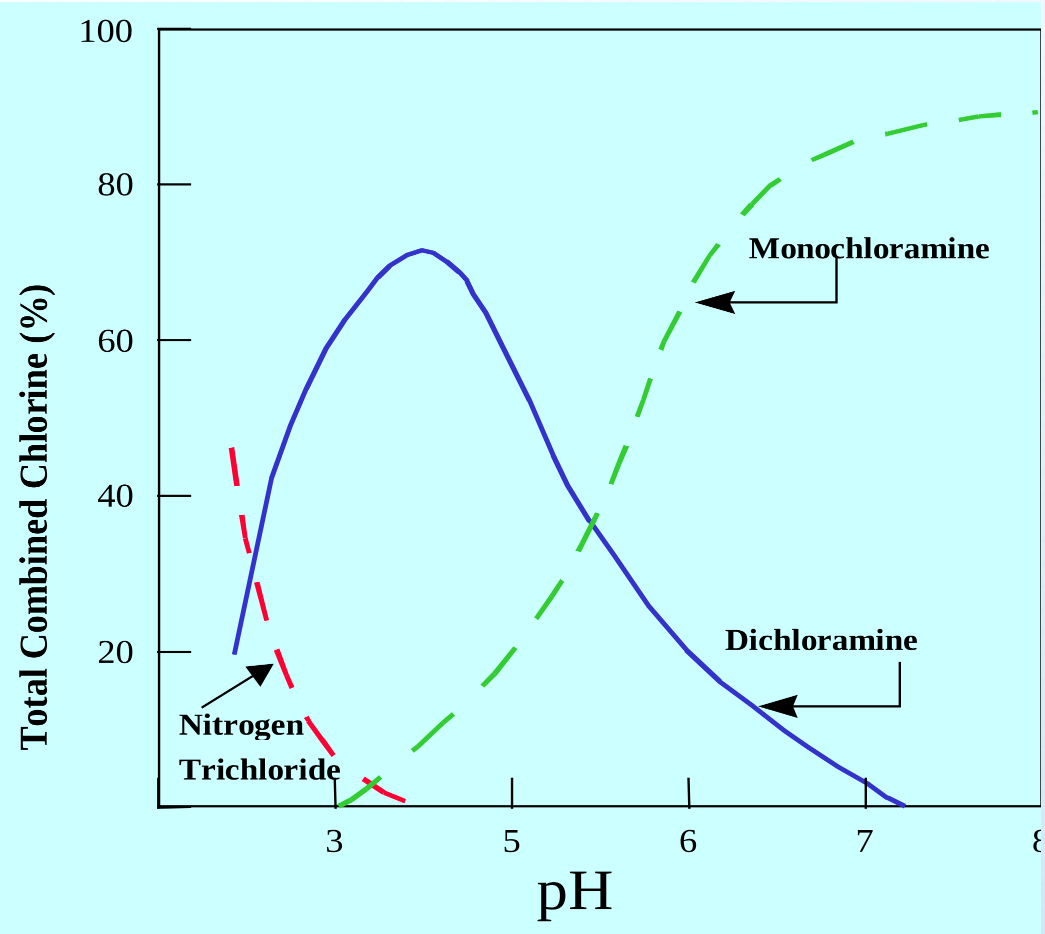
#$k_{25} = 8.3 \times 10^5\ M^{-2}s^{-1}[NH_2Cl][Br^-][H^+]$

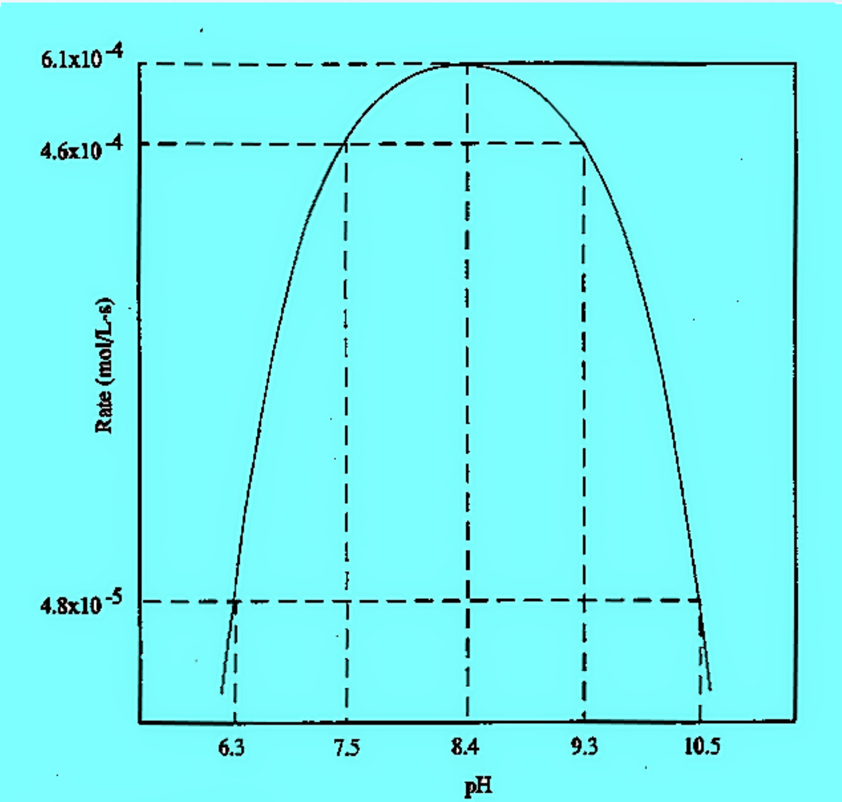
Breakpoint Chlorination

The Chlorine/Nitrogen ratio effects chloramine speciation

Target Ratio in Practice is 3:1 to 5:1 mg Cl_2 / mg NH_4-N







Source: Snoeyink and Jenkins 1980

Figure 3.4 Rate of monochloramine formation as a function of pH.

pH 8.3 to 8.4 is commonly
used as the optimum target for monochloramine
formation at a Cl_2:NH_4 -N mass ratio of 3:1 – 5:1

Chloramination is an All or Nothing Proposition

Free Chlorinated Water

Chloraminated Water

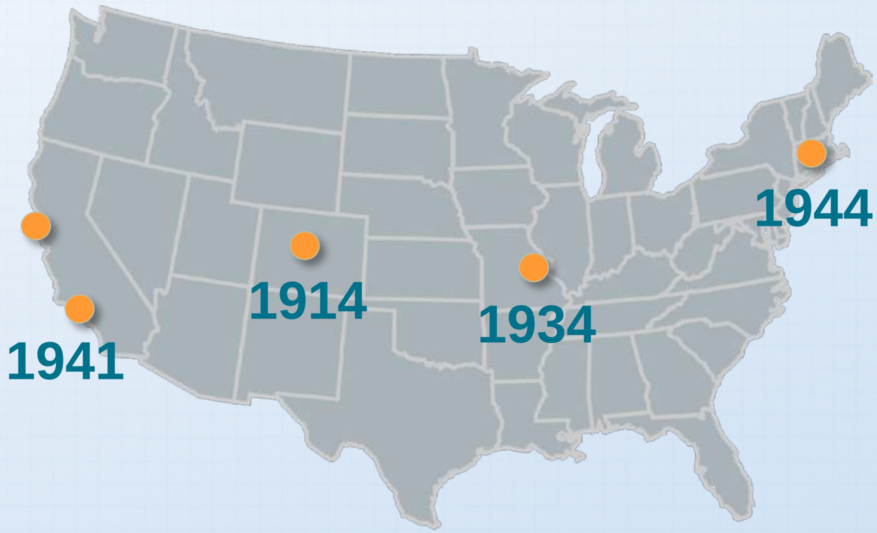
Breakpoint

Loss of disinfectant residual

Who Uses Chloramines ?

Who Uses Chloramine?

1. Metropolitan Water District of Southern California - 1941
2. Denver - 1914
3. St Louis - 1934
4. Boston – 1944
5. 29% of US Utilities (2007)



Advantages and Disadvantages of Chloramines

Advantages and Disadvantages of Chloramines

Advantages	Disadvantages
Controls DBP production (reductions of 40-80%)	Residual ammonia can lead to nitrification
Reduces taste and odor complaints	Possible increased elastomer degradation
Disinfectant residual persistence in distant parts of the distribution system	Health effects with sensitive customers
An established practice	Industrial process impacts
Ability to penetrate biofilms	Possible need for multiple injection points
	Produces known and unknown DBPs with unknown toxicity

Current DBPs

Regulatory Status

TTHM

Chloroform (TCM)

Bromodichloromethane (BDCM)

Dibromochloromethane (DBCM)

Bromoform (TBM)

HAA9

Regulated (HAA_5):

- Monochloroacetic acid (MCAA)
- Dichloroacetic acid (DCAA)
- Trichloroacetic acid (TCAA)
- Monobromoacetic acid (MBAA)
- Dibromoacetic acid (DBAA)

Unregulated:

- Bromochloroacetic acid (BCAA)
- Tribromoacetic acid (TBAA)
- Bromodichloroacetic acid (BDCAA)
- Dibromochloroacetic acid (DBCAA)

TTHM MCL = 80 µg/L

HAA_5 MCL = 60 µg/L

But, > 600 DBPs Have Been Indentified

Disinfection By-Products Associated with Chloramines

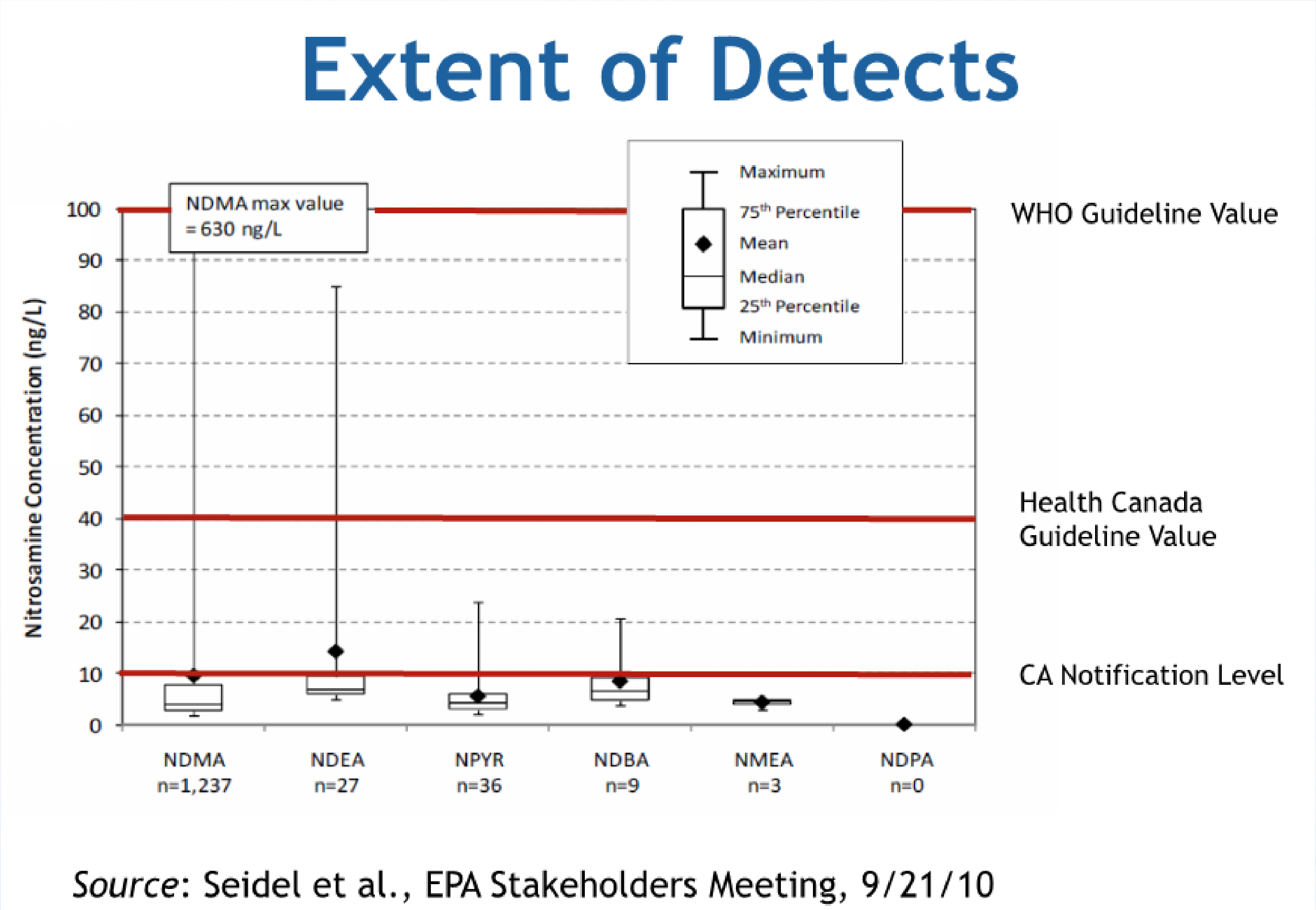
DBPs
Nitrosamines (e.g., NDMA)
Iodoacids
Hydrazine

Nitrosamine Occurence Data

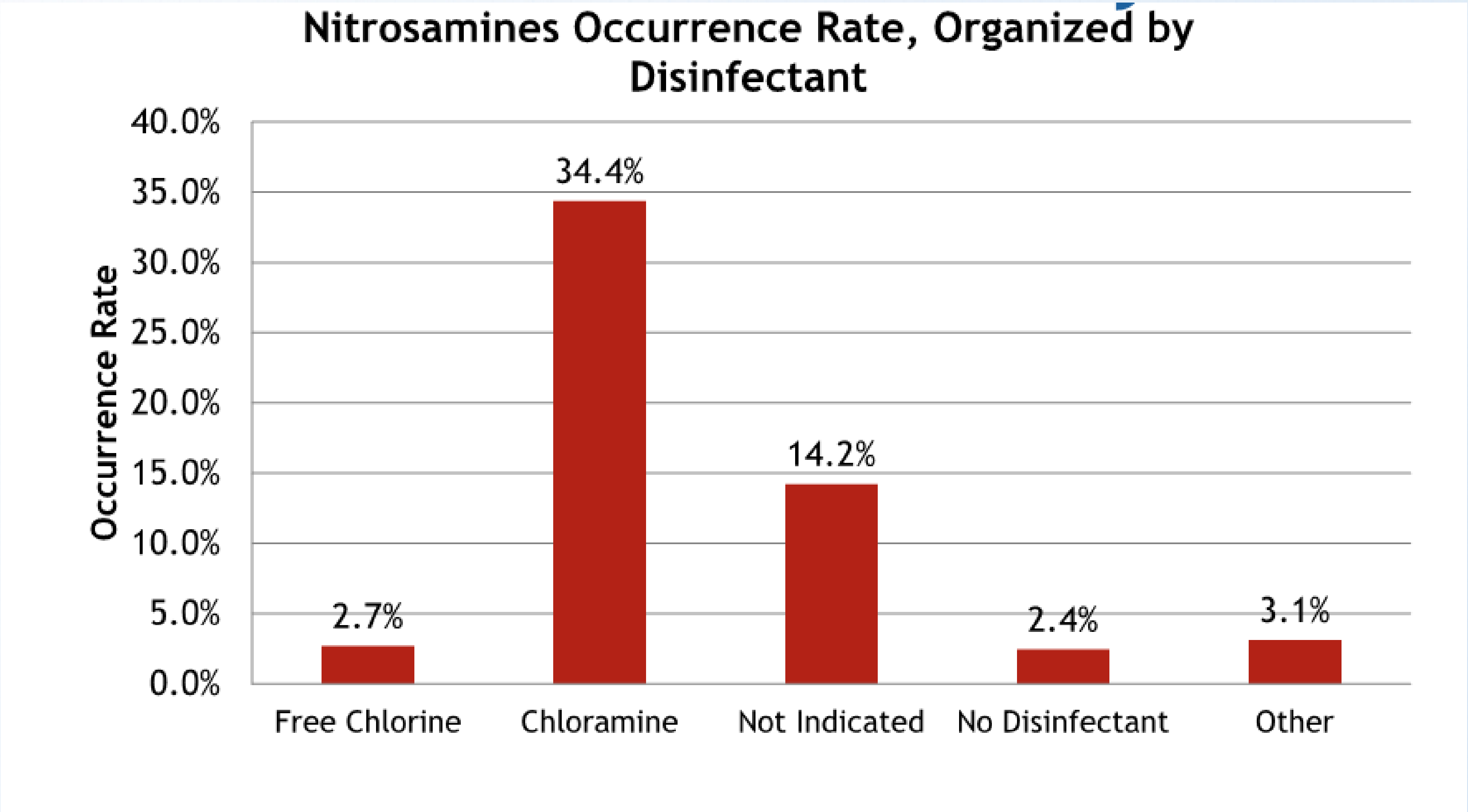
Nitrosamine	UCMR2 Data	
	Percent of **Samples** above the MRL (n = 13,280)	Percent of **Systems** with Samples above the MRL (n = 1,071)
NDMA	9.3%	24.6%
NDEA	0.2%	1.8%
NPYR	0.3%	1.6 %
NDBA	0.1%	0.5%
NMEA	0.0%	0.3%
NDPA	0.0%	0.0%

Source: Seidel et al., EPA Stakeholders Meeting, 9/21/10

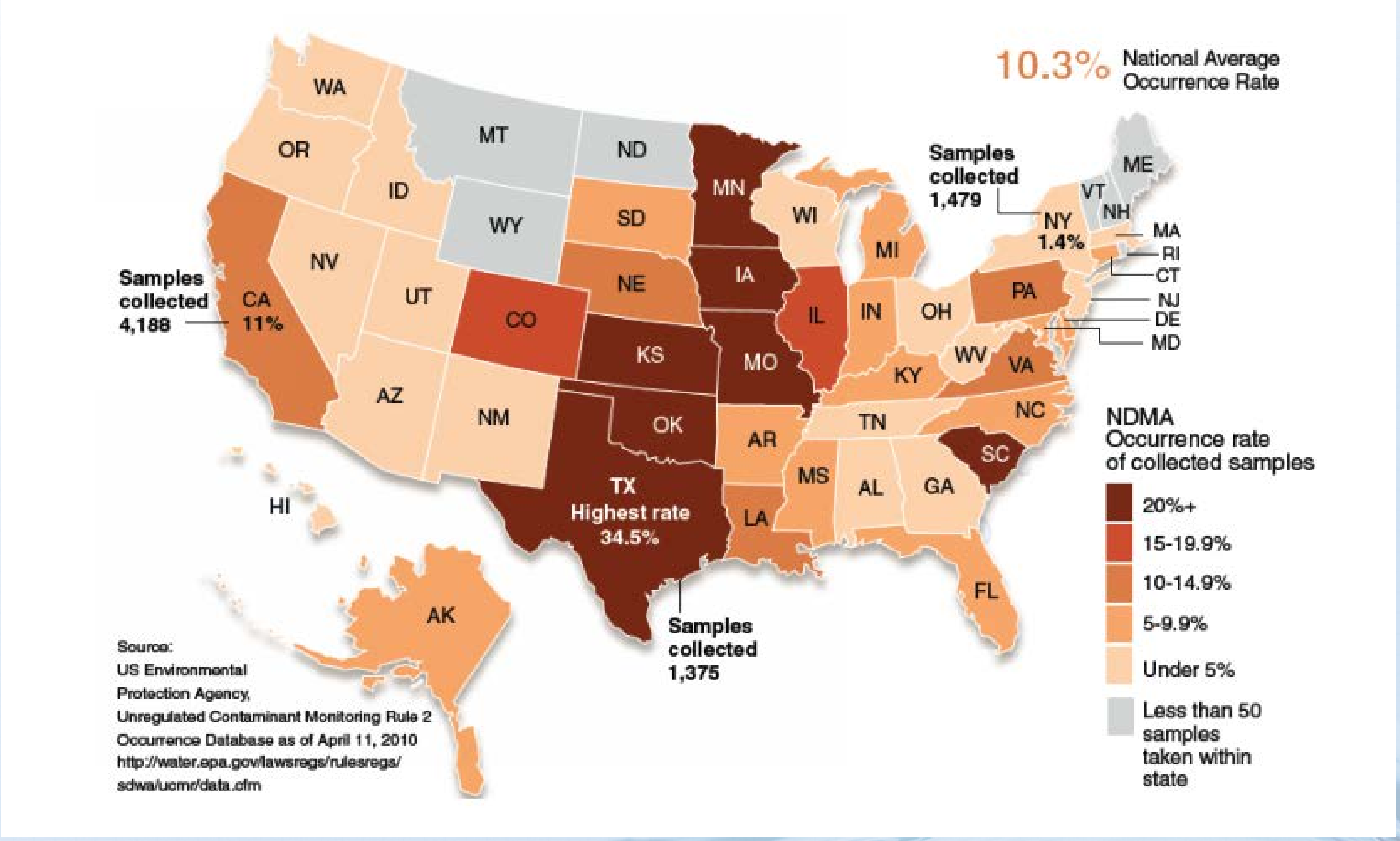
Range of Values for Nitrosamine



Nitrosamines Occur in Chloraminated Systems (UCMR2 Data)



Occurrence is Not Evenly Distributed

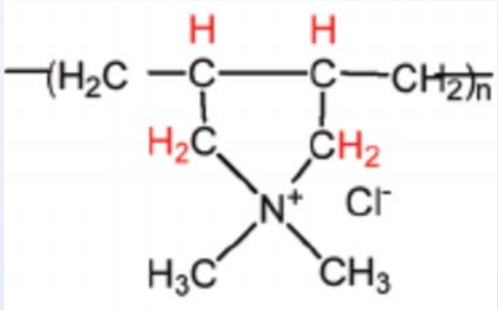


Pre-oxidation Effectively Destroys Watershed Derived Precursors

- Ozone > Chlorine > MPUV > LPUV > permanganate
  - Ozone – low CT
  - Chlorine – pH 8-9
  - Ozone/MPUV – higher pHs
- PAC/GAC
  - Removed watershed-derived precursors

Certain Polymers Can Contribute to NDMA Formation

- polyDADMAC



- Polyamine
- Polyamine-derived precursors also destroyed by oxidation
  – Low doses of polymers (≤ 0.8 mg/L) do not have significant impacts
  – PAC/GAC works on polyamine but not polyDADMAC

Iodinated Disinfection By-Products

- Iodine containing water are disinfected with chlorine or chloramines
  - Favored when ozone or chlorine is used as a pre-oxidant
  - Influenced by saltwater intrusion

Hydrazine

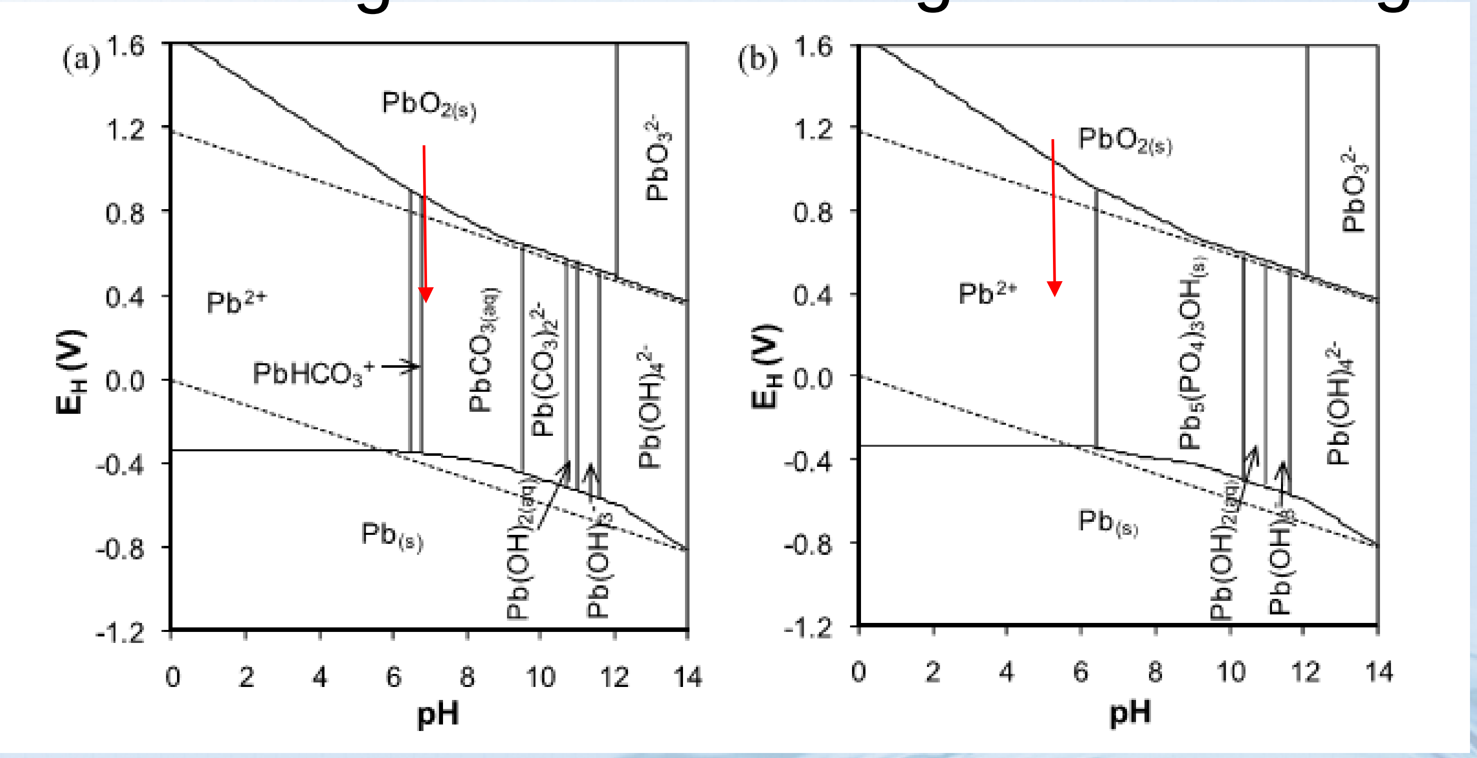
- Cancer risk (10^{-6}) at 10 ng/L
- Reaction of chloramine with ammonia
- Low when free ammonia is < 0.2 mg/L

- Computer model
  - pH< 9.9 and free ammonia<0.2 mg/L concentrations would be below 10 ng/L
  - pH=11 and free ammonia of 0.5 to 0.7 mg/L hydrazine concentrations ~ 100 ng/L

Lead and Copper Release

Reaction	EH 0 (V)
HOCl + 2e- + H+ ➡ Cl- + H2O	1.48
NH2Cl + H2O + 2e- ➡ Cl- + OH- + NH3	0.69

30 mg/L DIC 3 mg/L DIC + 3 mg/L OP



Source: Yanjiao Xie. 2010. Dissertation: *Dissolution, Formation, and Transformation of the Lead Corrosion Product PbO_2: Rates and Mechanisms of Reactions that Control Lead Release in Drinking Water Distribution Systems*. Washington University, St. Louis. http://openscholarship.wustl.edu/cgi/viewcontent.cgi?article=1386&context=etd

Passivation is Critical to Reducing Lead Levels

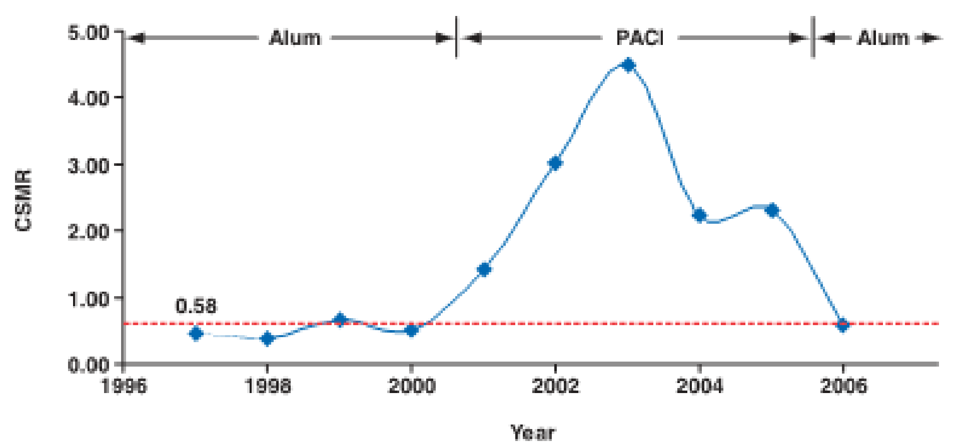
- Films
  - Calcium carbonate
  - Metal oxide
  - Metal carbonate
  - Phosphate/metal/carbonate

Many Factors Can Contribute to Metal Release

- Temperature
- pH/alkalinity
- ORP
- Disinfectant
- Dissolved oxygen
- Orthophosphate
- Polyphosphate
- Chloride
- Sulfate
- Pipe material
- Iron/Manganese
- Calcium

- Aluminum
- NOM
- Ammonia
- Hydrogen sulfide
- Silica

FIGURE 13 Historical plant data for the CSMR in Greenville, N.C., finished water

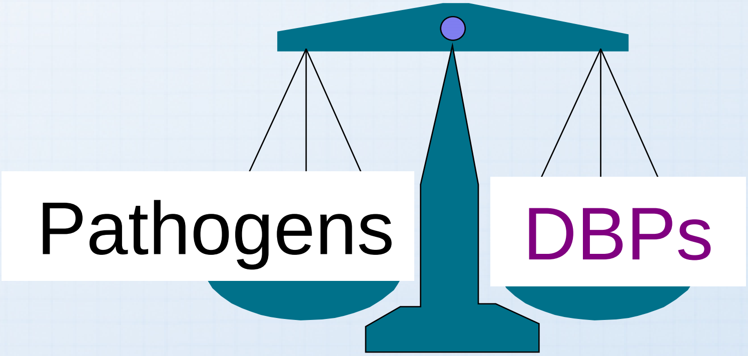


Edwards, 2007

DBP Formation

Problem Description

Cl_2 + NOM → Halogenated Organics

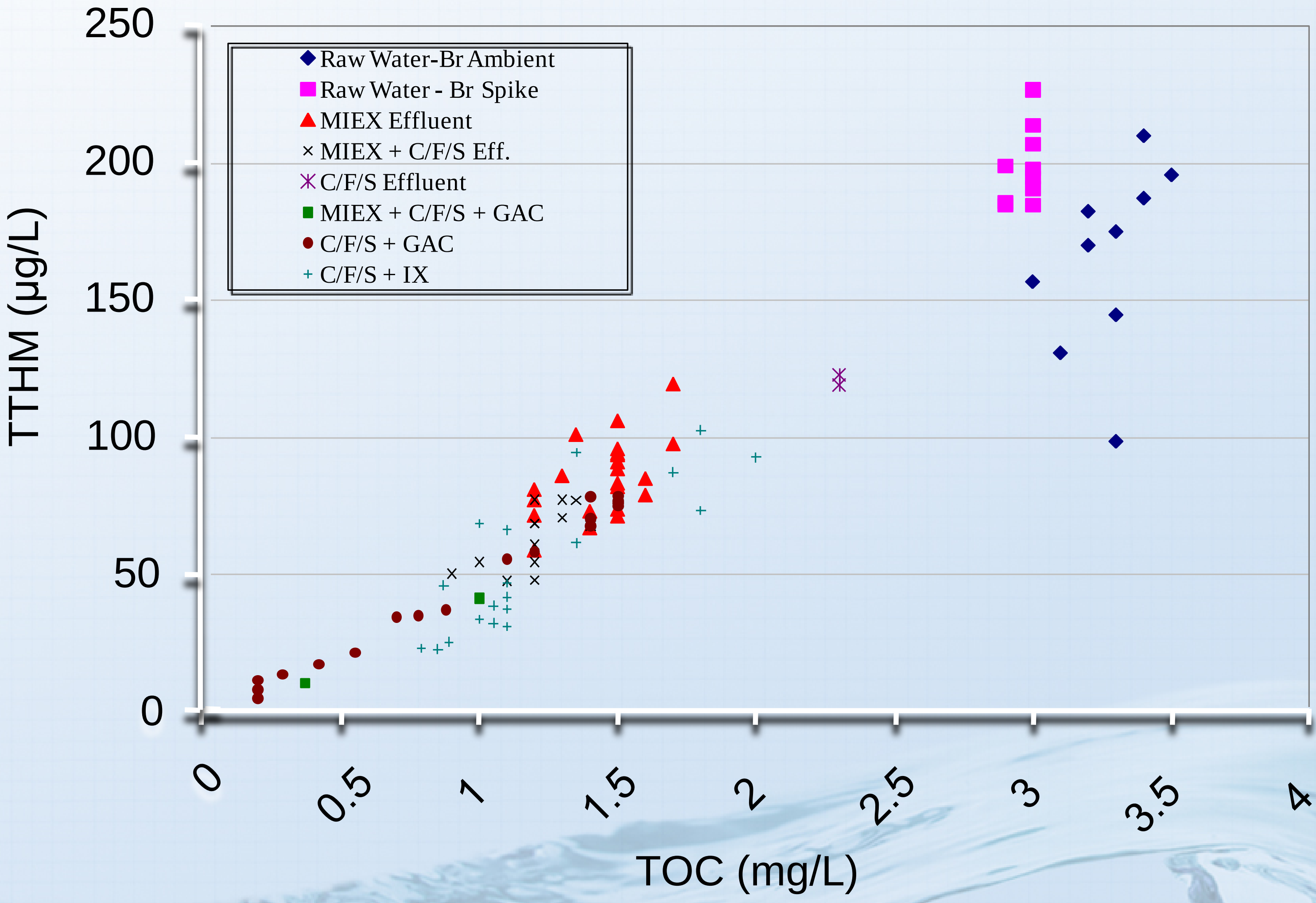


Factors for Disinfection / Disinfection By-Products

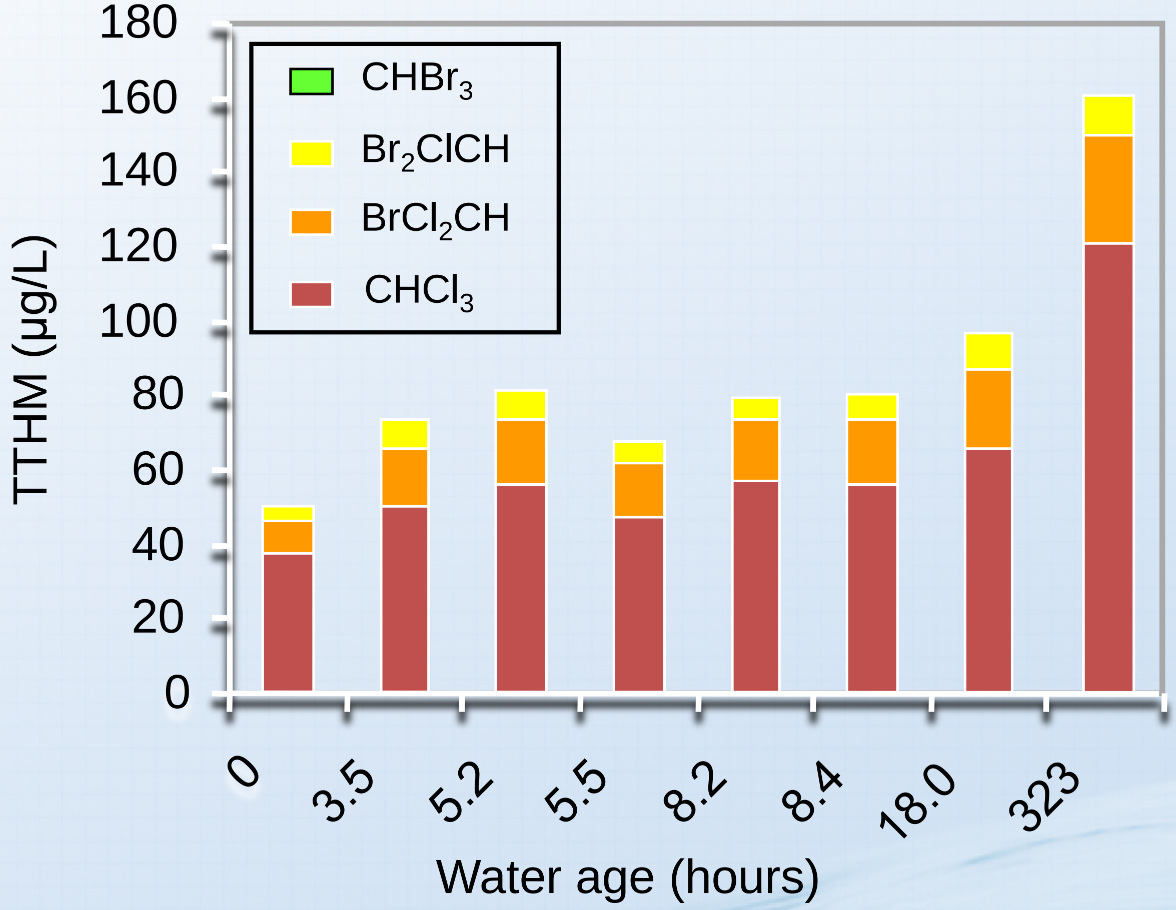
Water Quality
Disinfectant type and concentration
Bromide ion concentration
pH
Biomass (bulk water)
Water age
Natural organic matter
Temperature (kinetics)
Water treatment practices

Infrastructure
Biomass (biofilm)
Corrosion
Pipe material and diameter

DBPs Typically Increase With Increasing TOC



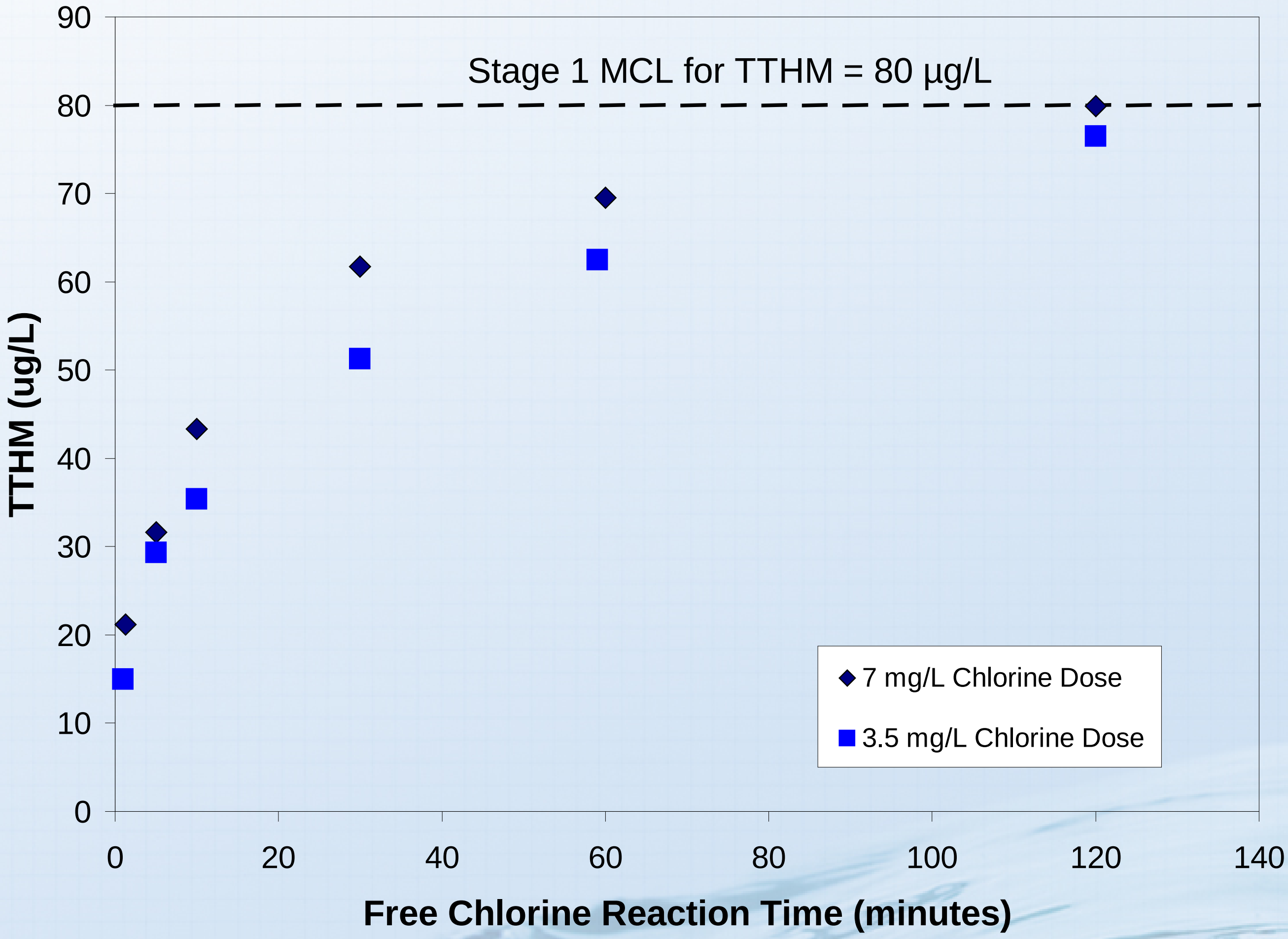
TTHMs Increase with Water Age



Formation and Decay of Disinfection By-Products in the Distribution System, Water Research Foundation Final Report, 2006.

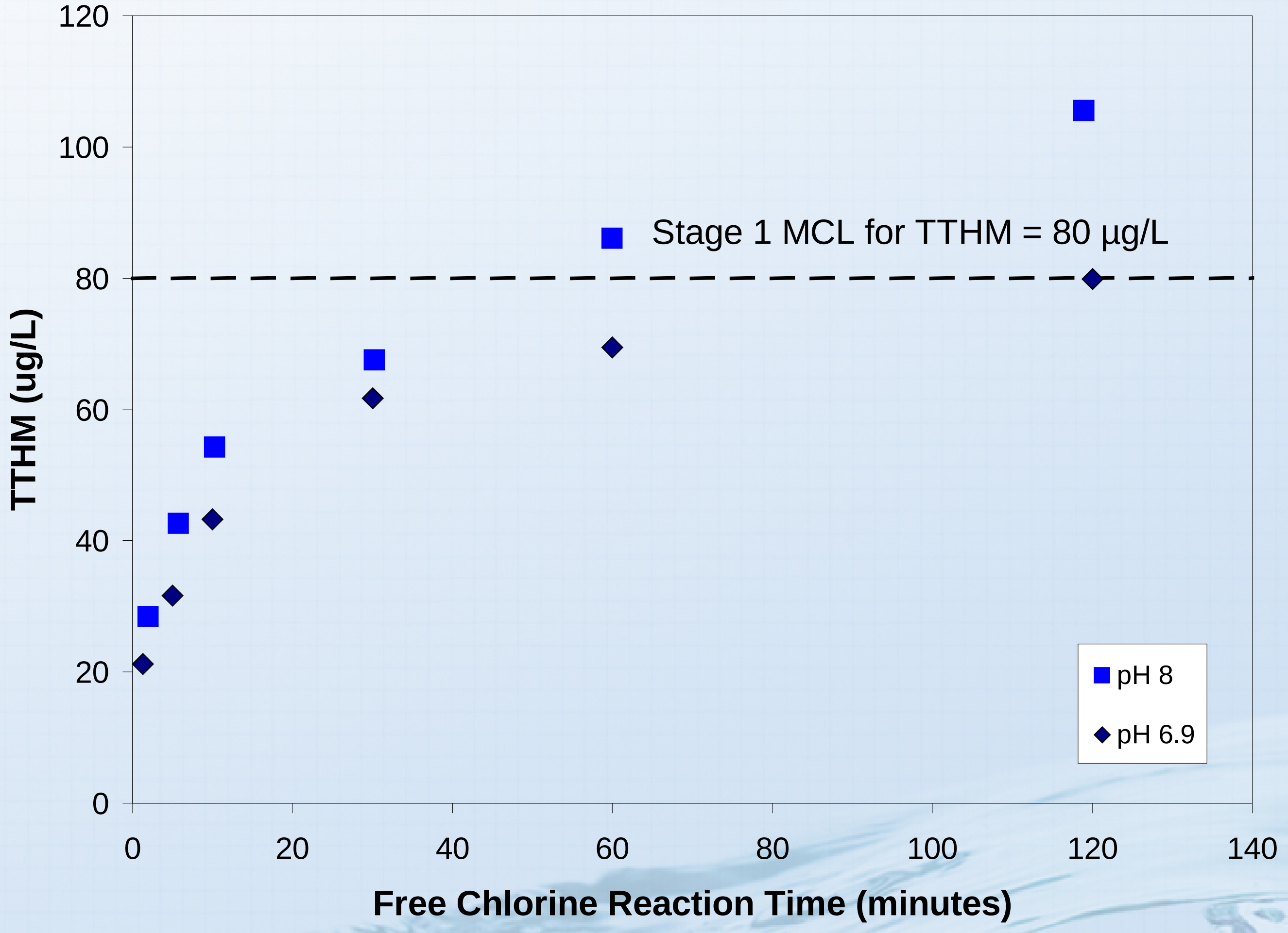
Effect of Chlorine Dose

TTHM Formation



Effect of pH

TTHM Formation



Controlling DBP Formation

Several Options are Available for Controlling DBPs

- DBP and DBP Precursor Removal Technologies
- Disinfection Alternatives

DBP and DBP Precursor Removal Technologies

Alternative	Advantages	Disadvantages
Enhanced Coagulation	• Low capital cost • Well understood technology	• Ineffective on some water • Increases sludge production
Granular and Powdered Activated Carbon	• Well-understood technology • May remove VOCs/SOCs	• Typically requires high EBCT (> 10 min.) • May require high change-out frequency (< 40 days) • Short contact times with PAC
O_3/Biofiltration	• No media change-out required • Minimizes TOC in DS	• O_3 may be expensive • Biofilm needs to be managed
Ion Exchange	• Can target multiple DBP precursors • Low EBCT (< 5 min.)	• Produces a waste brine • NDMA formation must be evaluated
Reverse Osmosis Nanofiltration	• Can target multiple DBP precursors and other contaminants	• Produces a waste brine • Very expensive
Air Stripping	• Can remove THMs in DS	• Limited to THMs and other volatile compounds

Disinfection Alternatives

Alternative	Advantages	Disadvantages
Chlorine Dioxide (Primary only)	• Does not form THMs or HAAs • Requires low CT values • Can achieve *Cryptosporidium* inactivation	• Expensive • Possible odor issue is residual is not controlled • Forms chlorite, requiring additional monitoring
Ozone (Primary only)	• May remove VOCs/SOCs • Can achieve *Cryptosporidium* inactivation	• Provides no residual in distribution system (DS) • May form bromate • Expensive
UV (Primary only)	• Can achieve *Cryptosporidium* inactivation	• Provides no residual in DS
Chloramines (Primary and Secondary)	• Can maintain stable residual in large DS • Minimizes THM and HAA formation	• Nitrification • Possible NDMA formation

Future DBPs

And > 50% are still unknown

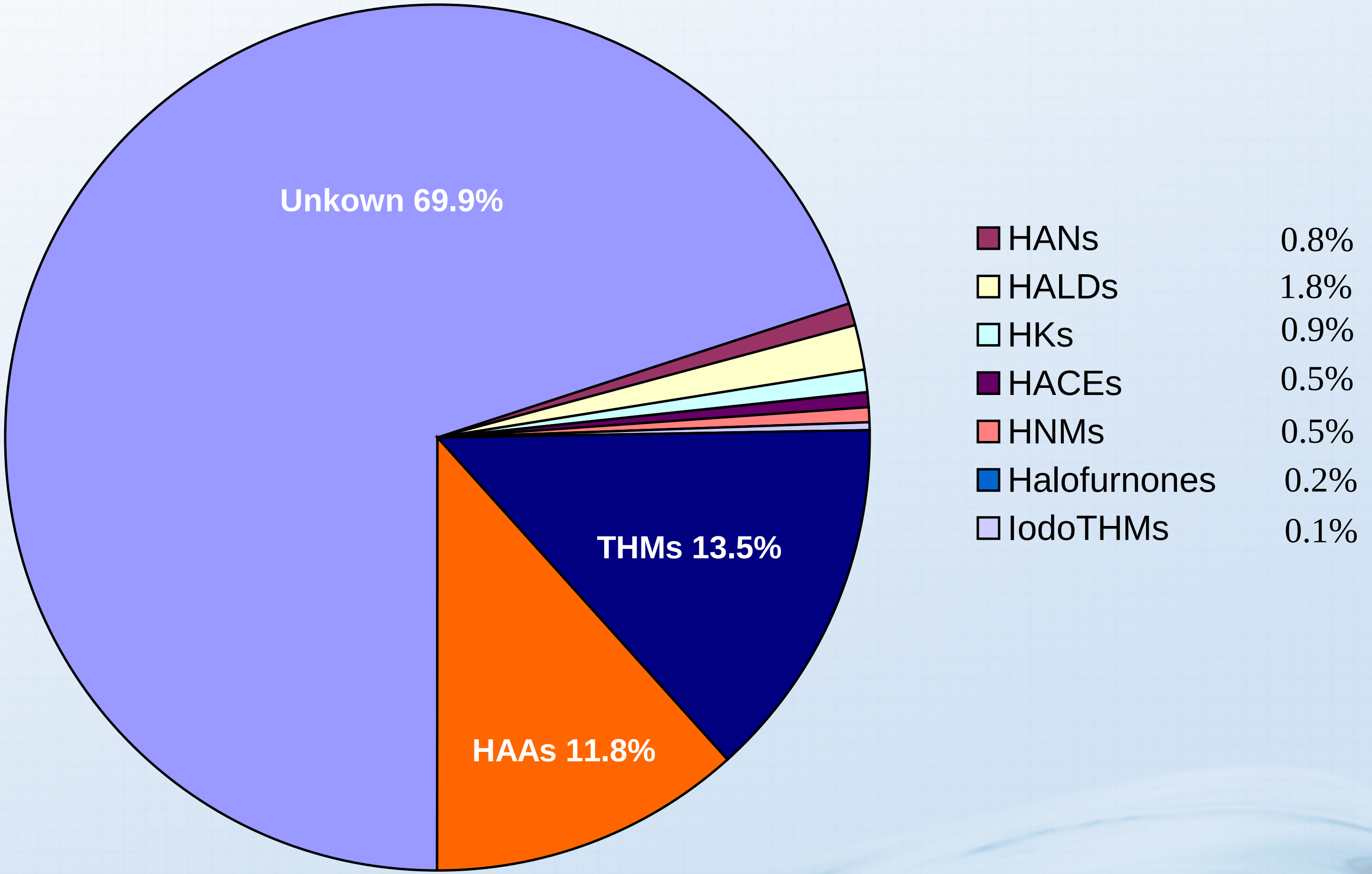


Figure adapted from Richardson et al., 2003

Several of emerging DBPs are on the EPA Contaminant Candidate List (CCL3)

1. 6 Nitrosamines (e.g., NDMA)
2. Formaldehyde
3. Bromochloromethane
4. Chlorate

Several of emerging DBPs are on the EPA Contaminant Candidate List (CCL3)

- 6 Nitrosamines (e.g., NDMA)
- Formaldehyde
- Bromochloromethane
- Chlorate

The 6 Nitrosamines are presently being screened as part of the Unregulated Contaminant Monitoring Rule (UCMR2)

NDMA

1. Chlorination
   a. Cationic coagulation polymers and coagulant aids (i.e., poly-DADMAC and epi-DMA)
2. Chloramination
   a. Formation is increased near breakpoint
   b. Preoxidation with chlorine or ozone may decrease formation
3. California Action Level = 10 ng/L

Nitrification

Occurrence of Nitrification

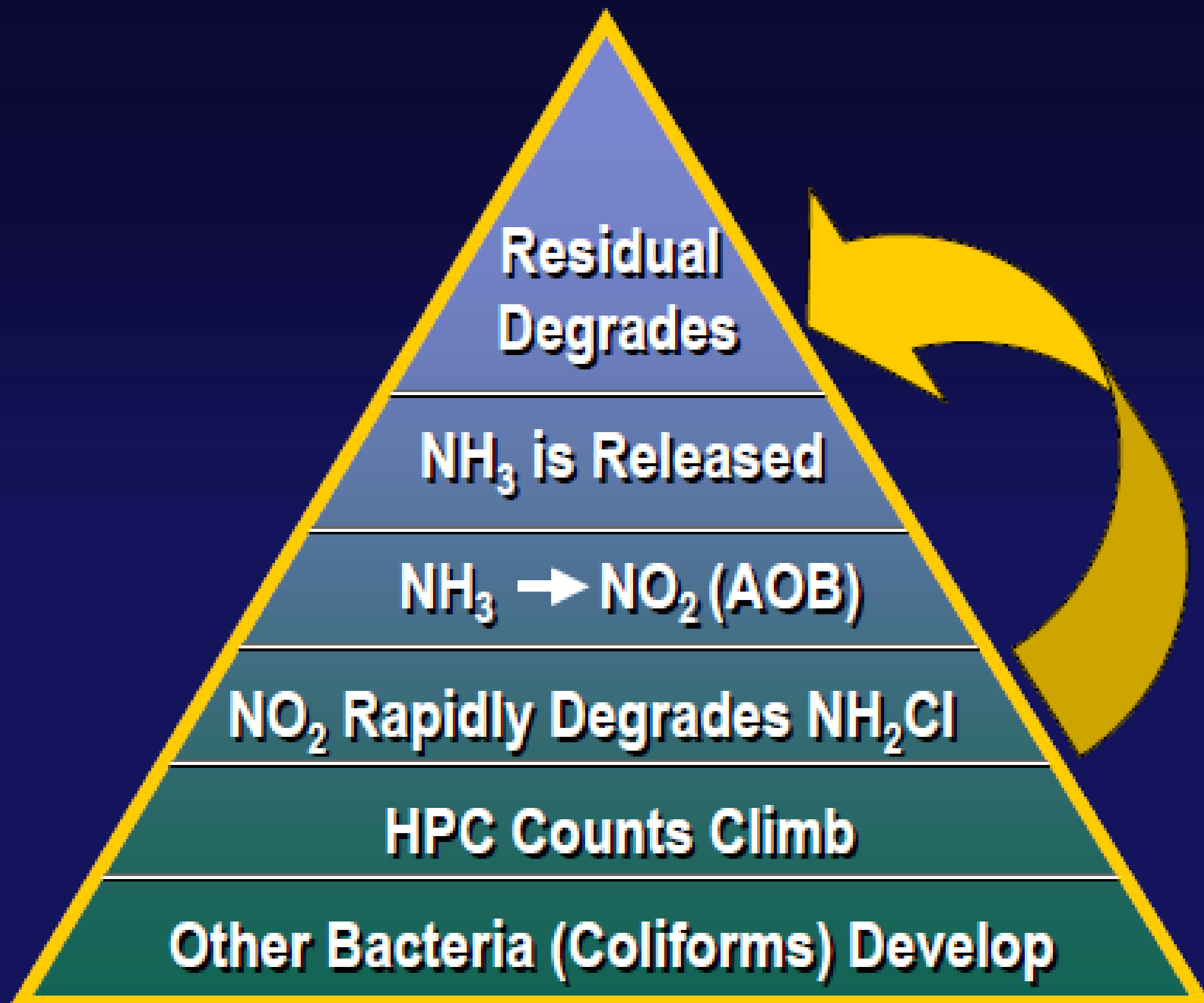
1. Nitrification may be occurring in 63% of utilities that use chloramines nationwide (1995)[1]
2. 48% of utilities surveyed nationwide experienced nitrification (2004)[2]
    a. 25% are responding to nitrification ≥2 times per summer
3. TCEQ found approximately 150 systems with potential nitrification issues, based on limited water quality results (2005)

1. *Kirmeyer et al., AwwaRF Report, 1995; Wilczak et al., Journal AWWA, 88:7:74, 1996*
2. *Kirmeyer et al., AwwaRF 2004*

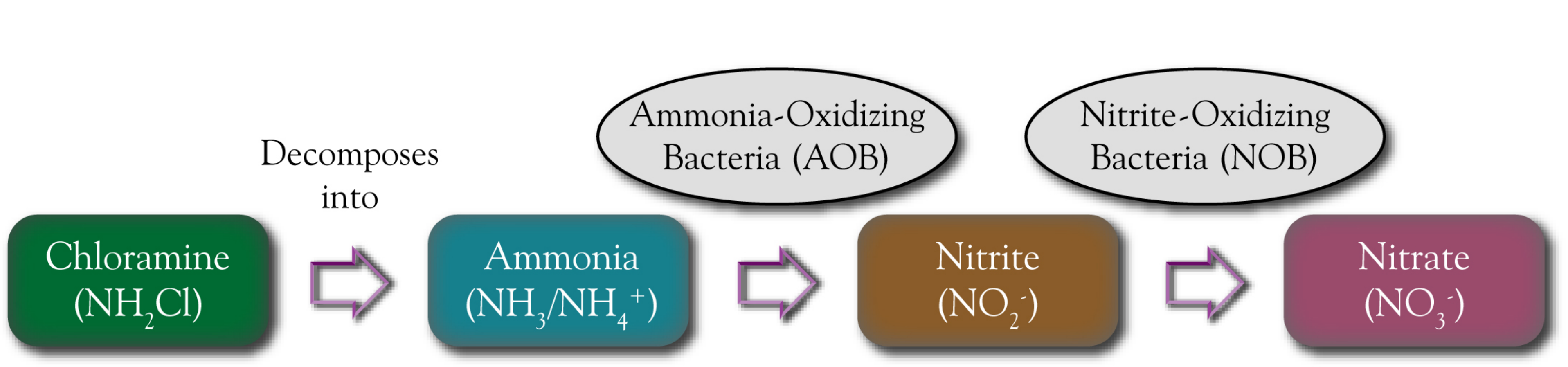
Why is Nitrification a Problem?

Issue	Potential Consequence
Decrease in disinfectant residuals	◆ Public Health Issues ◆ Compliance with Total Coliform Rule
High Heterotrophic Plate Counts (HPCs) with occasional coliform occurrences (*E. coli*)	◆ Public Health Issues ◆ Compliance with Total Coliform Rule (Boil orders) ◆ Loss of Consumer Confidence
May enhance corrosion of distribution piping	◆Pipeline Integrity ◆Replacement Cost

Problems Caused by Nitrification



Cause of Nitrification



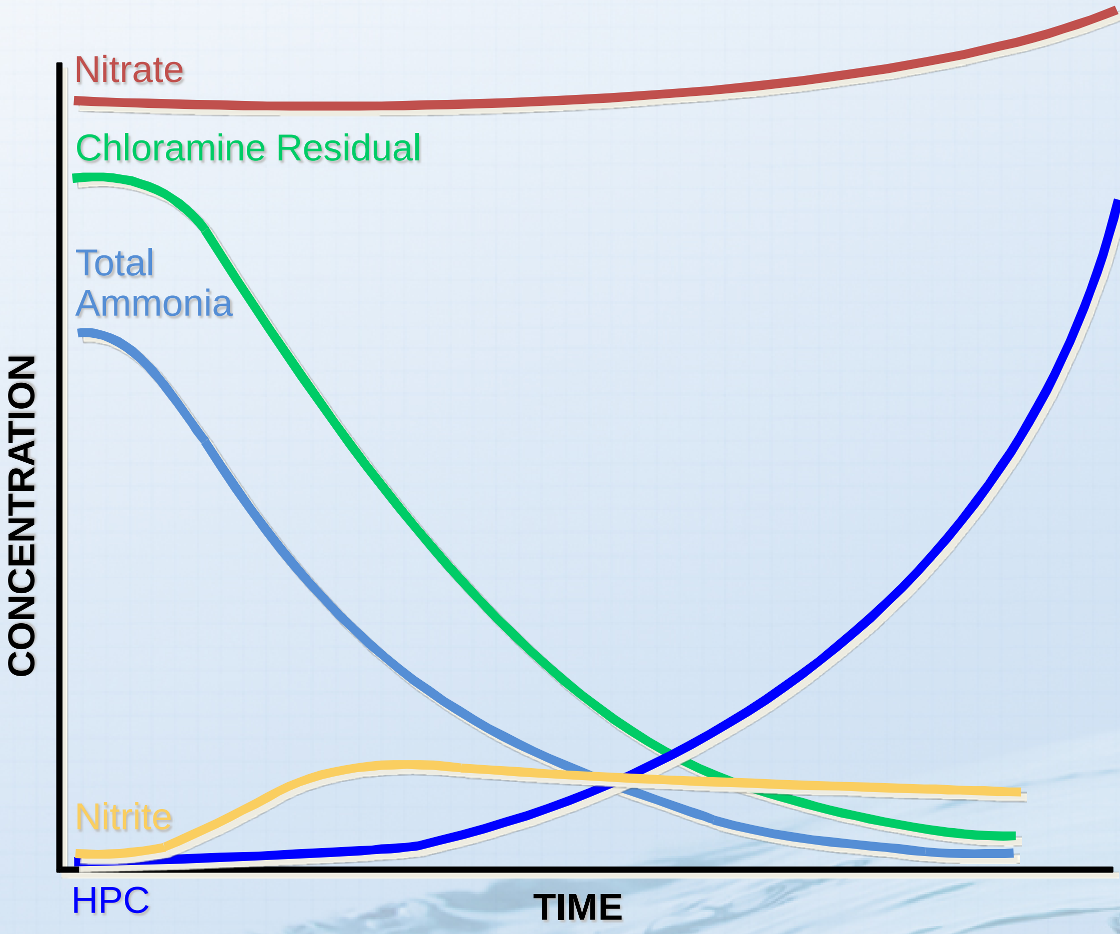
CarolloTemplateWaterWave.pptx

Favorable Conditions for Nitrification

Water Quality	
↑	Available Ammonia
↓	Monochloramine
↓	Chlorine-to-Nitrogen Ratio
↓	pH
↑	Temperature
↑	TOC

Distribution Sys. O&M	
↑	Water Age
↑	Accum. of biofilms and sediments
↑	Pipe Corrosion

Example Progression of a Nitrification Episode



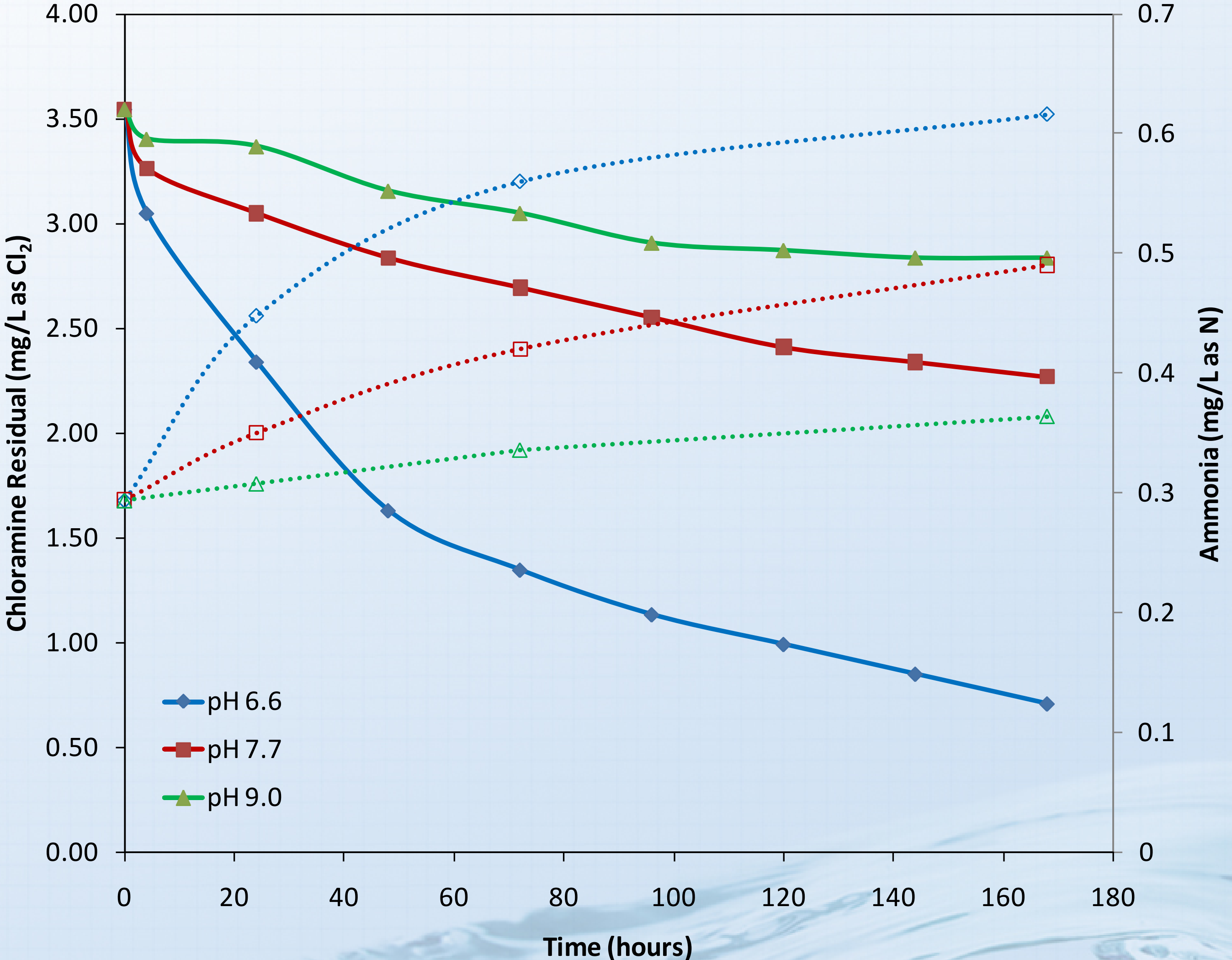
Nitrification Responses: Many Options

Action	Prevention	Correction
Adjust water quality	X	X
Flushing	Unidirectional	Conventional
Booster chlor(am)ination	X	
Free and breakpoint chlorination	X	X
Super-chlorination		X
Chlorite addition	X	
Cycling of storage facilities	X	Deep-cycling
Tank draining and disinfection		X

Nitrification Responses: Adjust Water Quality

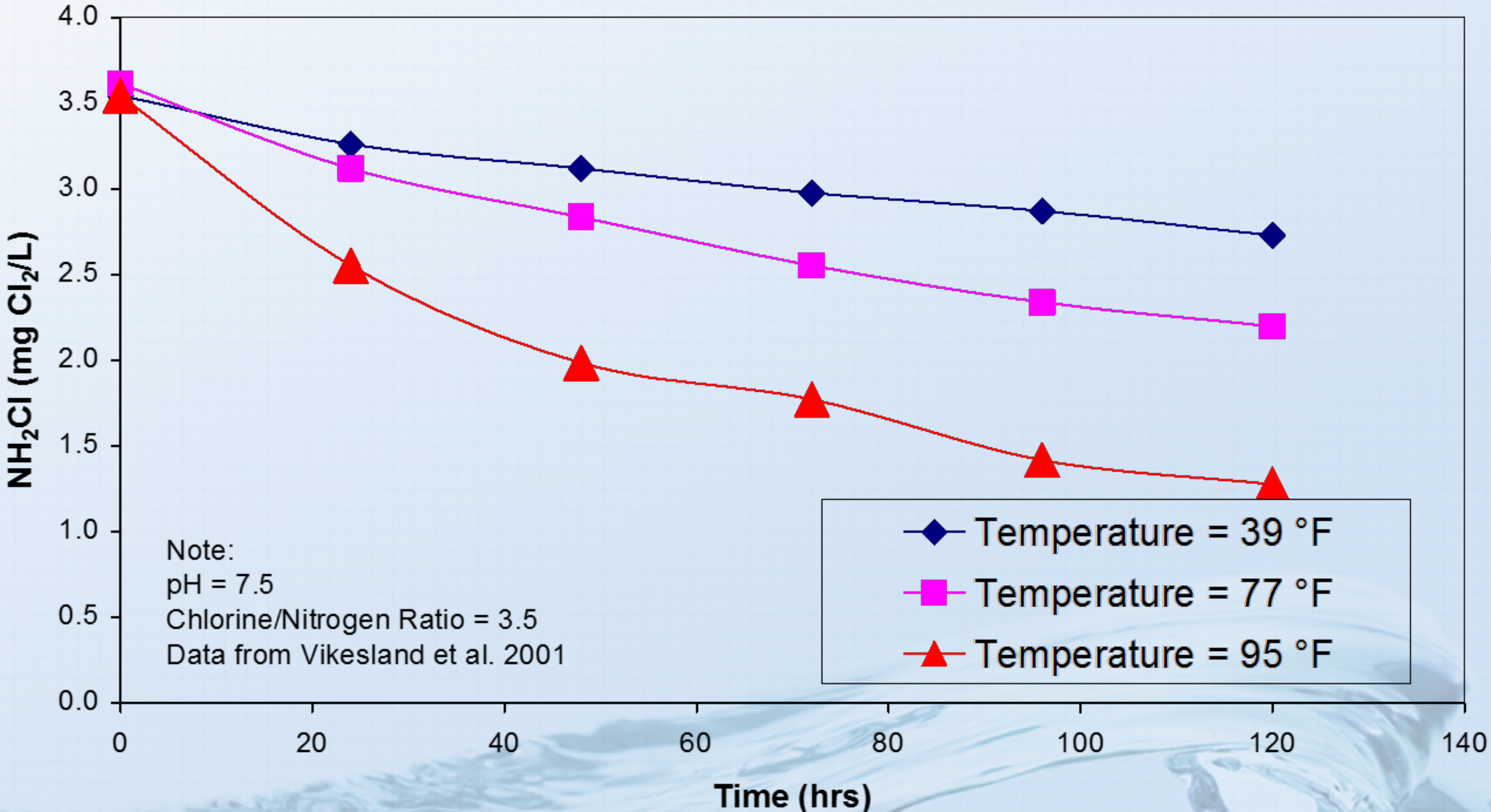
Parameter	Desirable
Free ammonia	<0.05-0.10 mg/L N
Total chlorine residual	2.0–3.0 mg/L at POEs >1.5 mg/L in the DS
Cl_2:NH_3-N ratio	4.5:1 – 5:1
pH	> 8.3 – 8.5
Limit NOM	System specific

Chloramine decay can release ammonia



Adapted from Duirk et al., 2005

Higher Temperatures Increase Chloramine Decay



Other Effects

Things that Chloramines Does not Affect

Cooking

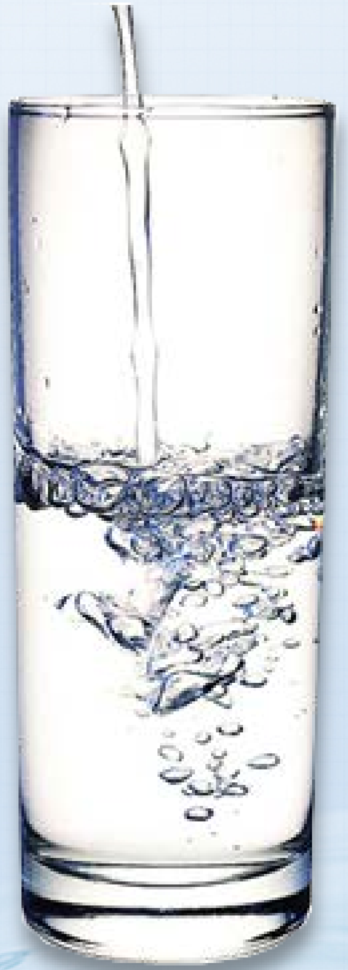
Cleaning
- Laundry
- Dishes
- Etc.

Washing

Gardening

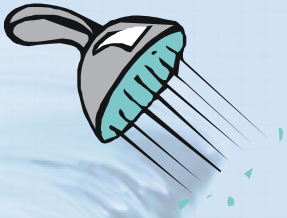
What Does Chloraminated Water Taste Like?

1. Chloramines typically do not impact any taste
2. In some cases, taste and smell of the water actually improves



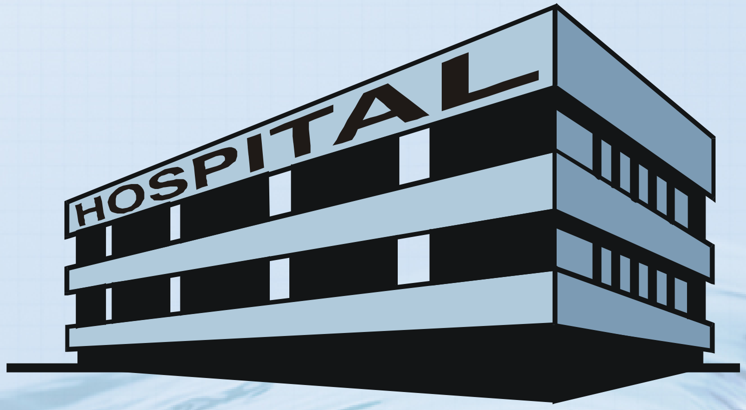
Will Chloraminated Affect Household Plumbing?

1. Washers and gaskets may tend to leak
   a. Toilets
   b. Faucets
   c. Water heaters
2. But, changes will be gradual if at all
3. Piping and other metallic parts should be fine



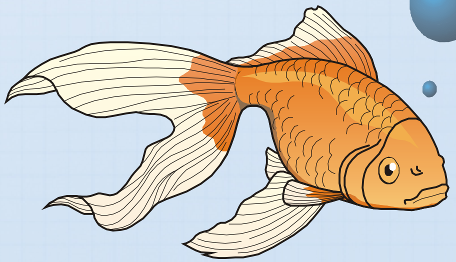
What Are the Concerns for Kidney Dialysis Patients?

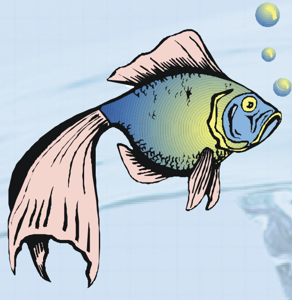
1. Chloramines (like chlorine) must be removed
2. Proper chemical addition and/or filtration is needed
3. Utilities would have to work with all hospitals and medical centers



Why Do Fish Owners Need to be Concerned?

1. Chloramines, like chlorine, is toxic to fish
    a. As they breathe the water
2. Chloramines are much more stable than chlorine
    a. It lasts in the water a lot longer than chlorine does
    b. Will not be removed by sunlight

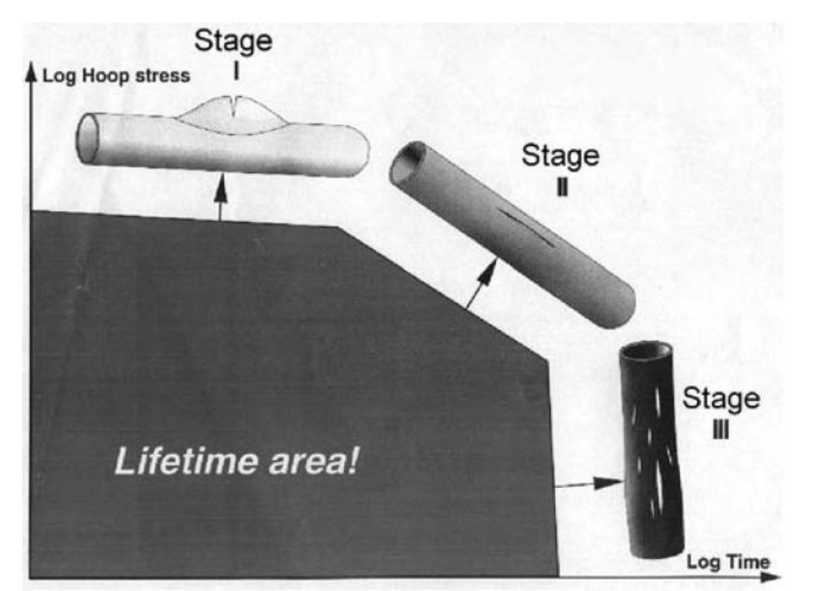




Evaluating the Compatibility of Chemical Disinfectants with Plastic Pipe Materials Used for Potable Water Distribution

1. Desktop study to evaluate the effects of disinfectants on PE and PVC pipe
2. Stage 3 failure of PE may be caused by disinfectants: ClO_2 > Cl_2 > ClA
3. The presence of disinfectants may increase the strength of the PVC inner wall
4. ASTM and AWWA standards provide no guidance to account for the use of disinfectants on plastic pipe
5. Caution is recommended in using plastic pipe in the design of water distribution systems

Three General Failure Modes of Pipe



Source: ASTM F 2263

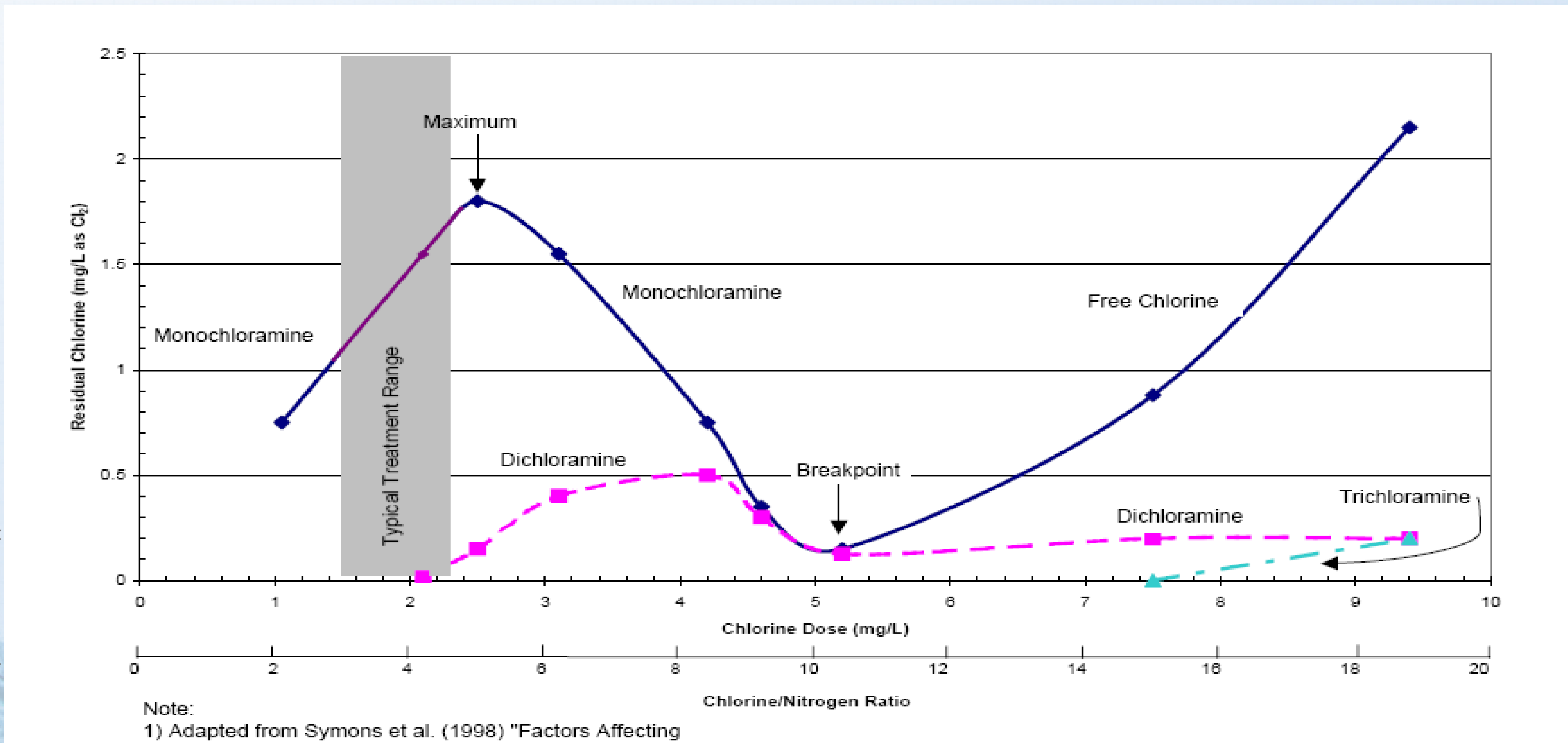
Chloramine-Related Challenges Can Be Overcome

Area	Challenge	Solution
Water Quality	Nitrification/bacterial growth High water age Ammonia release Bromochloramine	Unidirect. flushing prog. and reservoir cleaning Control water age Monitor water quality Nitrification action plan
Infrastructure	Material degradation: • Reacts with older (20 yrs.) or low quality elastomers	Identify increases in unaccounted-for water Replace failed components with chlora. resistant ones
Consumers	Health impacts: • Kidney dialysis patients • Fish and amphibians Negative impact to ultrapure water users	Identify key affected groups Public education Internal education

Free Chlorine Burn Conversion

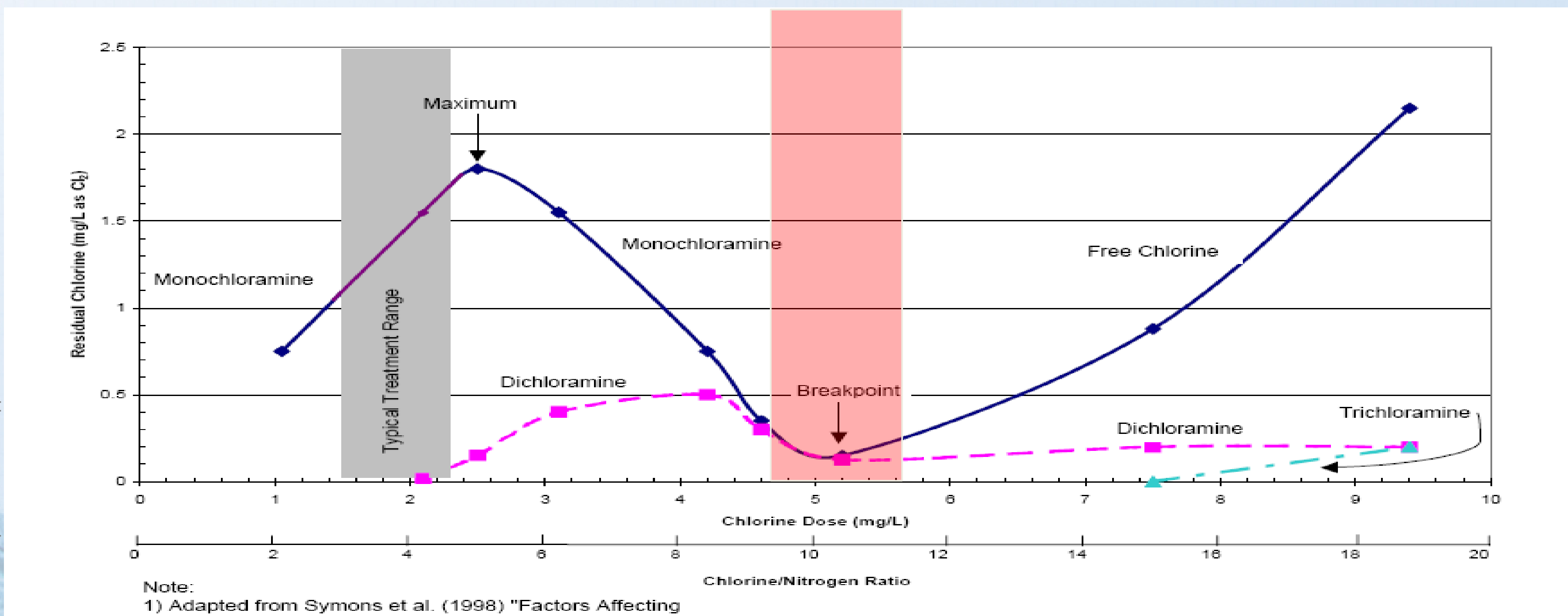
Steps for Transitioning from Chloramine to Free Chlorine (and Back)

- Concerns
  - Mixing of chlorinated and chloraminated water – loss of residual



Loss of Residual

- Occurs when
  - Chlorine doses are high
  - Large amounts of chlorinated water are mixed with small amount of chloraminated water



Solution

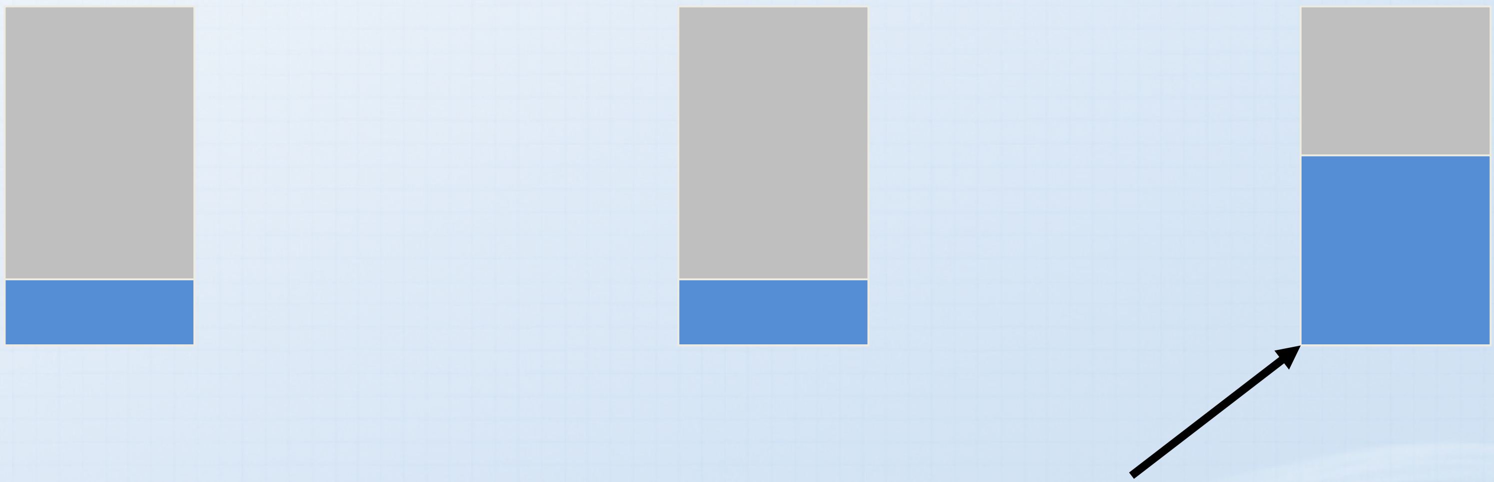
- Move water (either free chlorine or chloraminated water) out of the system first
  - Minimize mixing
  - Reduces the amount of time that low residual occurs

Steps

- chloramines

- free chlorine

- Minimize Storage Volume

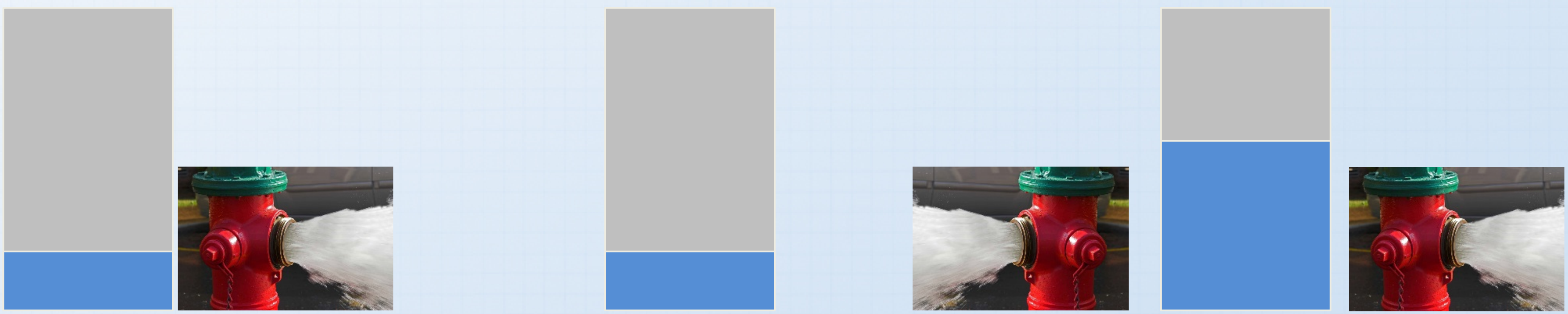


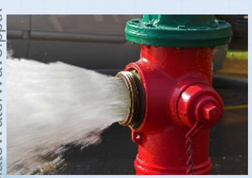
Probably need one reservoir ½ or more full (Fire flow/emergency)

Steps

- chloramines
- free chlorine

- Start Flushing hydrants (3 or 4 locations)



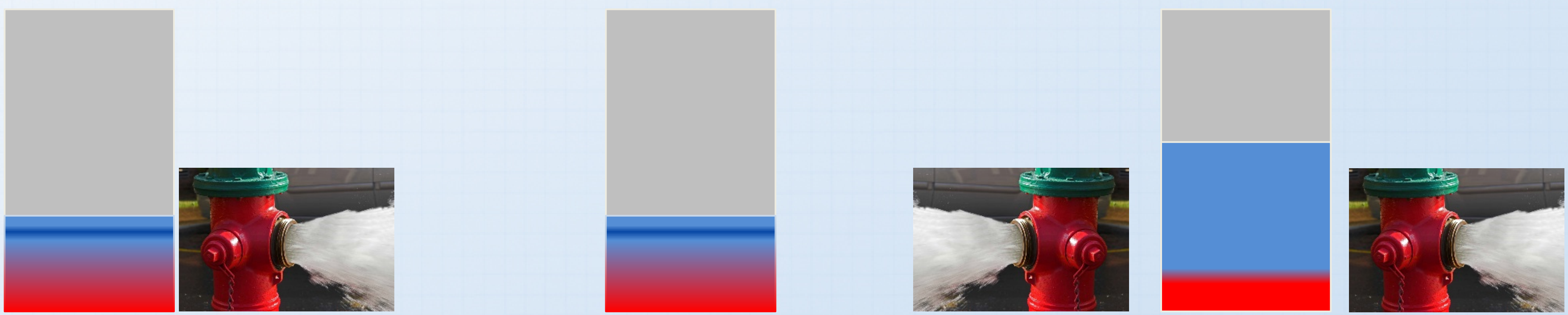


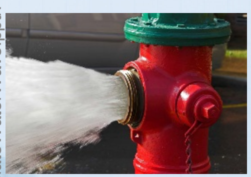
Steps

- chloramines

- free chlorine

- Monitoring residual





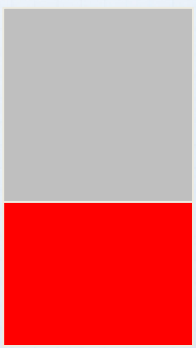
Sample tanks and plant

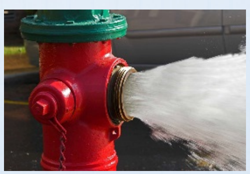
Steps

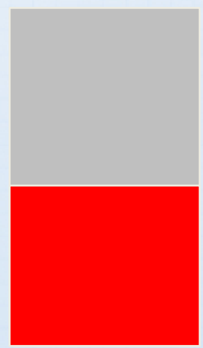
- chloramines

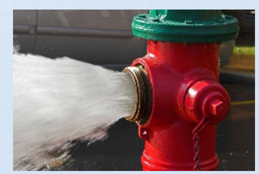
- free chlorine

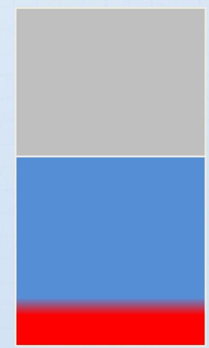
- Refill Low Tanks ASAP

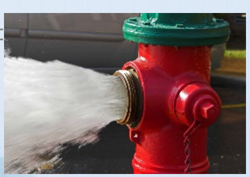










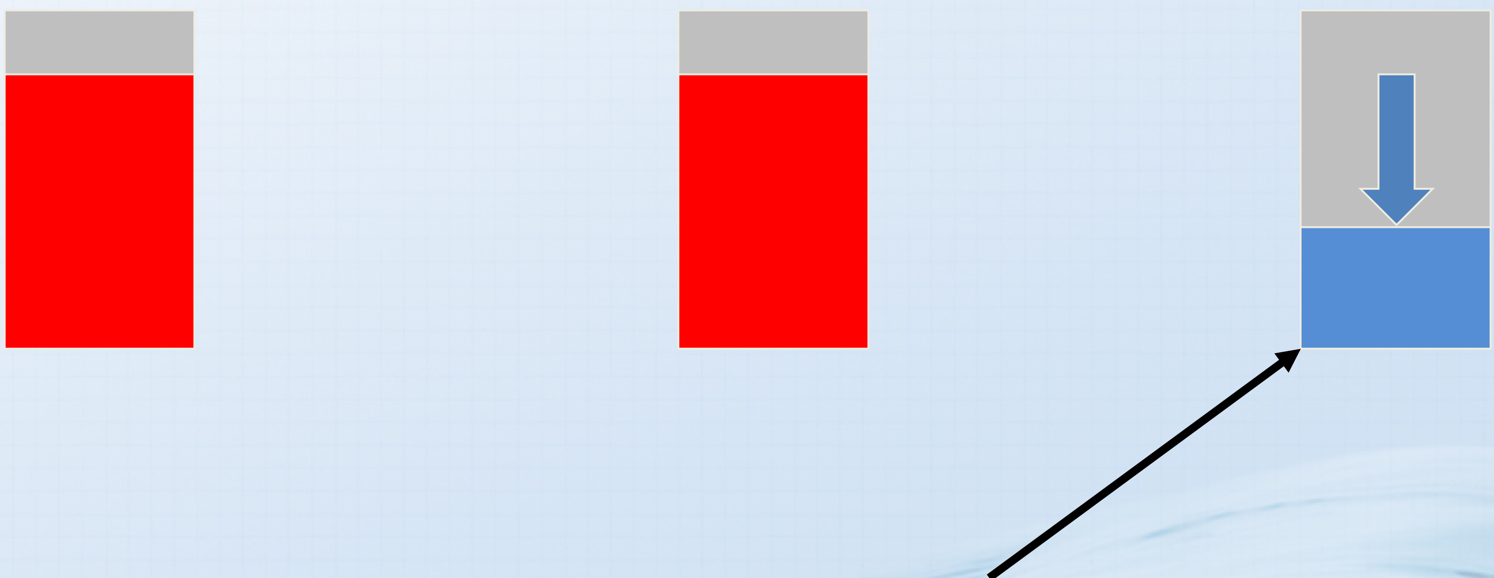


Steps

- chloramines

- free chlorine

- Drain Original Tank ASAP

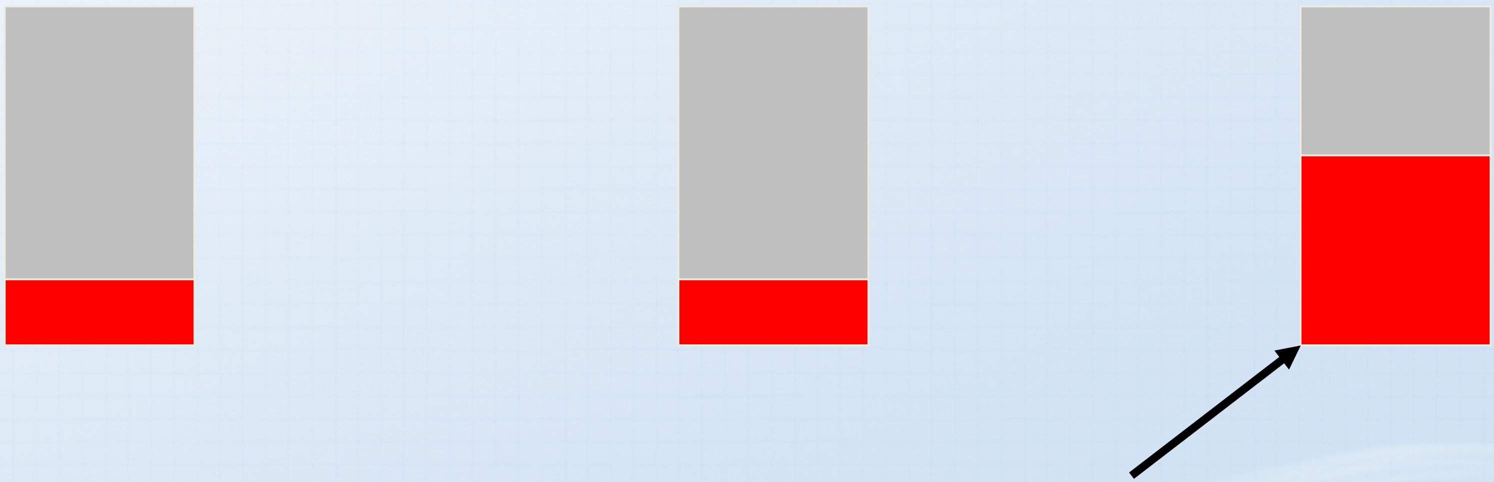


Once empty stop flushing
(check limits of the system)

Conversion Back (reverse)

- chloramines
- free chlorine

- Minimize Storage Volume



Probably need one reservoir ½ or more full (Fire flow/emergency)

Questions

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